

## Green electroluminescence from an ionic iridium complex

Jason D. Slinker, Cheong Y. Koh, and George G. Malliaras<sup>a)</sup>

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

Michael S. Lowry and Stefan Bernhard

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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We report green emission from a single-layer device based on the ionic transition metal complex  $[\text{Ir}(\text{F-mppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$ , where F-mppy is 2-(4'-fluorophenyl)-5-methylpyridine and dtb-bpy is 4,4'-di-tert-butyl-2,2'-bipyridine. External quantum efficiencies of up to 1.1% are achieved with air-stable contacts, and up to 1.8% with a CsF/Al top contact. Addition of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was found to improve the device response time and cause a bias-dependent shift in the emission spectrum. As a result, electroluminescence was observed at 531 nm (CIE coordinates: 0.3230 and 0.5886), the lowest wavelength reported to date for a device based on ionic transition metal complexes. © 2005 American Institute of Physics.

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A recent concept in solid-state electroluminescent devices involves the use of ionic transition metal complexes (iTMCs).<sup>1-8</sup> These devices differ significantly from conventional organic light emitting diodes due to the presence of mobile ions in the organic film. A prototypical example of an iTMC is the ruthenium complex  $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$  (where bpy is 2,2'-bipyridine). An electroluminescent device is fabricated by sandwiching a thin (~100 nm) film of  $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$  between two metal contacts. Upon application of a bias, and according to the electrodynamic model,<sup>9,10</sup> the counter ions ( $\text{PF}_6^-$ ) redistribute and create high electric fields near the contacts. Electrons and holes are subsequently injected into the metal complexes  $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ , migrate towards each other by means of hopping, and recombine within a single metal complex to produce light. Electroluminescent devices based on iTMCs offer ease of fabrication, as they consist of a single layer of organic that is deposited from solution.<sup>7</sup> In addition, contrary to conventional OLEDs that require low work function cathodes, they show efficient operation even with air-stable cathodes.<sup>11</sup> This enables fabrication by means of lamination,<sup>12</sup> as well as the development of fault-tolerant architectures for large-area illumination panels.<sup>13</sup>

Any new class of electroluminescent devices must show emission throughout the visible part of the spectrum, a key requirement for full color displays and illumination quality lighting. The vast majority of iTMC-based devices reported to date utilize complexes of ruthenium or osmium and emit in the red part of the spectrum.<sup>1-7</sup> Neutral complexes of iridium have been utilized in OLEDs as emitters (dispersed in a charge transporting organic matrix), and are known to emit efficiently in the red, green, and blue part of the spectrum.<sup>14-16</sup> However, it was not until 2004 when an ionic iridium complex,  $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$ , where ppy is 2-phenylpyridine and dtb-bpy is 4,4'-di-tert-butyl-2,2'-bipyridine, was first employed to fabricate electroluminescent devices.<sup>8</sup> These emitted in the yellow part of the spectrum, which represents the lowest emission wavelength

available in an iTMC-based device. Green and blue emission have yet to be achieved.

In this letter, we report a green iTMC-based electroluminescent device. The active layer is the ionic Ir complex  $[\text{Ir}(\text{F-mppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$ , where F-mppy is 2-(4'-fluorophenyl)-5-methylpyridine (see Fig. 1), in which the strong inductive and mesomeric effects of the fluoro-substituent on the phenyl ring (*meta* to the site of coordination) are responsible for the blueshifted emission over previously reported iTMCs.<sup>17-19</sup>  $[\text{Ir}(\text{F-mppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$  was targeted to be an effective electroluminophore while examining a series of F-mppy iTMCs that were prepared by combinatorial methods.<sup>17</sup> We discuss the performance of devices with various top contacts, and demonstrate that addition of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{BMIM}^+(\text{PF}_6^-)$ ) leads to enhancement of device performance.

The ligand F-mppy was synthesized by refluxing a stoichiometric amount of 1-[2-(4-fluoro-phenyl)-2-oxo-ethyl]-pyridinium bromide with 2-methyl-2-propenal and excess ammonium acetate in methanol for 12 h.<sup>17,20</sup> The  $[\text{Ir}(\text{F-mppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$  complex was subsequently prepared following a modified literature procedure.<sup>8,17</sup> The ionic liquid  $\text{BMIM}^+(\text{PF}_6^-)$  was purchased from Aldrich (Fluka) and used as-received. Sandwich-type devices were fabricated by dissolving the Ir complex in HPLC grade acetonitrile at a concentration of 24 mg/mL, and spin coating onto glass substrates covered with prepatterned ITO contacts (Thin Film Devices, Anaheim, CA) at 1000 rpm. For devices incorporating ionic liquid, 1.5  $\mu\text{L}$  of  $\text{BMIM}^+(\text{PF}_6^-)$  were added per

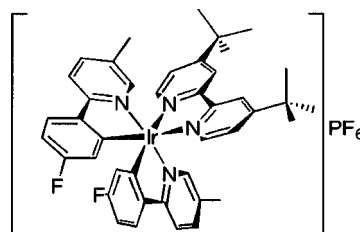


FIG. 1. Chemical structure of  $[\text{Ir}(\text{F-mppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$ .

<sup>a)</sup>Electronic mail: ggml@cornell.edu

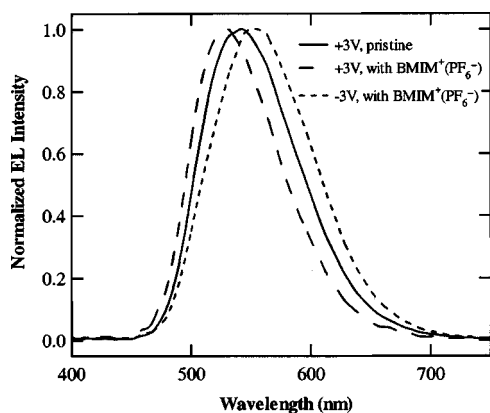


FIG. 2. EL spectra for the ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au devices with (dashed lines) and without (solid line) the ionic liquid BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>).

mL of solution. This amount was close to the upper limit, before phase separation became visible with an optical microscope. The preparation of the solutions and the casting of the films were performed inside a nitrogen glove box. The thickness of the films was between 70 and 80 nm, as measured with profilometry. The ITO substrates were cleaned just before the deposition of the organic layer by a deionized water bath, followed by UV/ozone treatment. The films were taken out of the glove box and dried for ~12 h at 80 °C under vacuum. They were then reintroduced in the glove box for further processing and characterization. The top contacts consisted of a 200 Å thick Au film, or a 10 Å thick CsF film capped with a 200 Å thick Al film. They were deposited through a shadow mask that defined six devices per substrate, each with a 3 mm<sup>2</sup> active area. The deposition of Au was carried out intermittently to minimize heating of the organic film. The electrical characteristics of the devices were measured with a Keithley 236 source-measure unit, and the emission was collected with a calibrated UDT S370 optometer coupled to an integrating sphere. The EL spectra were measured with a calibrated S2000 Ocean Optics fiber spectrometer.

The electroluminescence (EL) spectrum of an ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au device under +3 V bias (ITO positive with respect to Au) is shown as a solid line in Fig. 2. The spectrum, which peaks at  $\lambda_{\text{max}}=542$  nm (CIE coordinates 0.3678 and 0.5777), represents the lowest wavelength of emission observed in an iTMC device. The spectrum was found to be independent of bias (+3 V and -3 V), and was the same in devices with a CsF/Al top contact. It was also found to be the same as the photoluminescence spectrum in acetonitrile solution, which indicates that the same mechanism is responsible for emission in both cases. From the above it is clear that the fluorine substituents on the phenylpyridine ligands cause a blueshift of the emission spectrum relative to the nonfluorinated complex, which phosphoresces at 558 nm.<sup>8</sup>

The luminance and efficiency of [Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>) devices were found to depend on the direction of the bias, as well as on the choice of top contact. Devices with Au top contacts showed rectification and efficiencies that were higher in reverse than in forward bias: At +3 V, emission was weak, with a luminance of 15 cd/m<sup>2</sup> and a quantum efficiency of 0.15%. However, at -3 V the luminance reached 110 cd/m<sup>2</sup>, and the quantum efficiency reached 1.1%. With a CsF/Al top contact, the luminance and

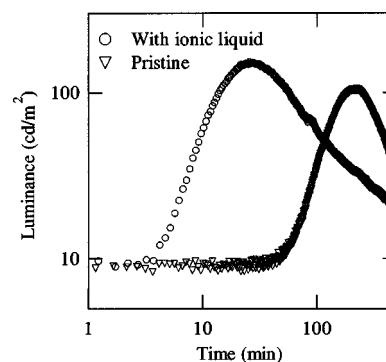


FIG. 3. Temporal evolution of the radiant flux in two ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au devices, one with a pristine film and the other containing the ionic liquid BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>).

quantum efficiency +3 V were 170 cd/m<sup>2</sup> and 1.8%, respectively. These devices did not show any emission under reverse bias due to electrochemical degradation of the CsF/Al contact.

In [Ru(bpy)<sub>3</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> devices, the accumulation (depletion) of PF<sub>6</sub><sup>-</sup> counter ions near the positive (negative) contact causes large electric fields that decrease the tunneling barrier<sup>9,10</sup> and assist the injection of holes (electrons) in [Ru(bpy)<sub>3</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub>. These fields are high enough to make the ITO and Au contacts ohmic for both electron and hole injection.<sup>11</sup> As a result, no substantial rectification is observed in ITO/[Ru(bpy)<sub>3</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub>/Au devices. The rectification observed in the ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au devices indicates that the electric field caused by the accumulation of PF<sub>6</sub><sup>-</sup> near the Au contact is not enough to decrease the barrier for electron injection to the point where the contact is made ohmic. Using a contact with a lower work function than Au, such as CsF/Al, or ITO (reverse bias data), results in improved electron injection and higher device efficiency. This image is consistent with the fact that the device efficiency varies in the same order as the work function (WF) of the contacts (WF<sub>CsF/Al</sub> < WF<sub>ITO</sub> < WF<sub>Au</sub>). A similar rectification was observed in the nonfluorinated Ir complex.<sup>8</sup>

Consistent with the electrodynamic mechanism of operation,<sup>9,10</sup> the devices show long turn-on times. As shown in Fig. 3, the turn-on time (time to reach maximum luminance) of the ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au device at -3 V is about 4 h. This is consistent with previous observations in the nonfluorinated Ir complex.<sup>8</sup> A significant reduction in turn-on time, to ~40 min, was achieved by using the lower work function CsF/Al contact. This is due to the fact that fewer PF<sub>6</sub><sup>-</sup> counter ions need to be displaced in order to make the CsF/Al contact an efficient electron injector. However, this contact is not as inert and air stable as Au, which compromises one of the chief advantages of iTMC-based devices. Clearly, an alternative means of improving turn-on time is desirable.

According to the electrodynamic model,<sup>9,10</sup> the turn-on time is dictated by the ionic conductivity and should decrease if extra mobile ions are added to the iTMC layer. Ionic liquids have recently been used in polymeric semiconductors as a convenient way to increase the ion density.<sup>21-23</sup> Figure 3 shows the influence of the ionic liquid BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>) in the temporal behavior of the luminance of an ITO/[Ir(F-mpy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au device. The introduction of ionic liquid decreases the turn-on time to 25 min. Although

the turn-on time is still too slow for practical applications, the decrease is dramatic and shows that ionic liquids are promising for improving response time. The introduction of ionic liquid also helps with the luminance, which increases to 150 cd/m<sup>2</sup> (at -3 V, see Fig. 3) and 20 cd/m<sup>2</sup> (at +3 V).

In addition to improved response time, devices with BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>) also showed interesting spectral behavior. Figure 2 shows that addition of the ionic liquid in an ITO/[Ir(F-mppy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>)/Au device causes a bias-dependent shift in the electroluminescence spectrum. Namely, the spectrum of these devices peaks at 531 nm (+3 V) and at 560 nm (-3 V). A similar bias dependent shift has been observed in the electroluminescence spectrum of the nonfluorinated Ir complex,<sup>8</sup> and it is not understood at present. A more complete study of the effects of BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>) on Ir device performance is underway.

In conclusion, we demonstrated green emission in devices based on a single layer of the ionic transition metal complex [Ir(F-mppy)<sub>2</sub>(dtb-bpy)]<sup>+</sup>(PF<sub>6</sub><sup>-</sup>). External quantum efficiencies of up to 1.1% are achieved with air-stable contacts (ITO and Au), and up to 1.8% with a CsF/Al contact, with a corresponding luminance of 110 and 170 cd/m<sup>2</sup>, respectively. Addition of the ionic liquid BMIM<sup>+</sup>(PF<sub>6</sub><sup>-</sup>) improved the device response time dramatically. Furthermore, it produced a blueshift in the forward bias electroluminescence peak to 531 nm, the lowest emission wavelength reported to date for a device based on an ionic transition metal complex.

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